

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Method of Making Foundry Sand Moulds and Cores

We, F. & M. SUPPLIES LIMITED, a British Company of 9 Hayne Street, London, E.C.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of making foundry cores and moulds.

The base of foundry mould and cores is sand and/or other refractory materials and one or more binders which, by setting or curing, bond the sand particles together.

Two principal factors to be taken into account in selecting a suitable binder are the speed of setting and the strength of the bond produced. The sooner the mould or core acquires sufficient strength to permit it to be stripped from its forming box, the greater number of moulds or cores can be produced from that box in a given period of time. Also, it is desirable that the mould or core will acquire sufficient strength for foundry use within a reasonable period of time and preferably without stoving.

Among conventional binders which are used are the drying oils such as linseed oil, China wood oil (tung oil), oiticica oil and blown fish oil. The mechanism of setting of these oils is not fully understood but it is believed to be a combination of oxidation and polymerisation. All of them in order to produce the required strength have to be subjected to cure at elevated (usually 200—250°C) temperatures for a considerable time, for example, from  $\frac{1}{2}$  to 3 hours or even more according to temperature, kind of oven and size of core. The setting of the drying oil does not take place at once; at the beginning, when the oil is warming up, its viscosity is

lowered and if other additives have not been mixed into the sand, the core will sag considerably or even collapse.

It is an object of the invention to provide a method of making foundry sand cores and moulds whereby the mould or core can be stripped from its forming box within a relatively short period of time and whereby sufficient bond strength can be obtained without curing at elevated temperatures.

Binders have been proposed previously in the foundry industry with a view to achieving this object such as for example sodium silicate and furan binders.

All have their limitations. The sodium silicate core is usually difficult to remove after casting. Furan binders are catalysed by strong acids and there are many foundry sands containing metallic oxides or salts which interfere with the setting reactions. Other refractory aggregates like olivine prevent the setting of furan binders. However the binders used in this invention can be employed with such sands when an organic binder is preferred.

In a method according to the invention for making a foundry mould or core sand and/or other refractory material is mixed with a binder and the mixture allowed to set. As the binder a blown drying oil and a polyisocyanate are used and the curing of the binder is catalysed by the use of two particular types of catalyst. During the setting, reaction of the hydroxyl groups of the drying oil with the isocyanate groups of the polyisocyanate occurs to form urethane linkages.

The selection of the appropriate amount of binder and catalysts i.e. the total weight of oil, polyisocyanate and catalysts present no

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difficulty to the man skilled in the foundry art. The amount of binder and catalysts will usually be from 1.0 to 2.5% by weight of the sand. Similarly, the amount of polyisocyanate used will vary with the different oils and the nature of the polyisocyanate. It will usually range from 20 to 50% by weight of the oil.

It is well known of course that polyisocyanates react with high molecular weight polyhydroxyl compounds to produce polyurethane polymers and these have been used for making foams and paint bases. However, if these polyurethane polymers are employed as binders in foundry sand compositions without stoving, the bond strength is insufficient even after prolonged setting. In contrast, the polymer produced by reacting a polyisocyanate with a hydroxylated drying oil will set, in the presence of suitable catalysts as hereinafter specified, to produce a bond of the required final strength. Furthermore, the rammed sand may be stripped from the box in some cases after only about 20 minutes at 15°C ambient temperature. It would appear therefore that in order to attain the desired bond both reactions i.e. drying of the oil and polyurethane formation have to take place.

It is possible to produce a weaker bond by using processed vegetable oil such as blown linseed oil, blown tung oil and blown dehydrated castor oil, in the presence of catalysts ("driers") like naphthenates of cobalt, manganese, lead, zinc and preferably also in the presence of an oxidizing agent. The strength of the mould or core may be sufficient for handling but will not be sufficient for casting for two reasons. In the first place, mechanically the sand is not strong enough to resist the flow of molten metal, particularly in relatively large castings of a section 4" and more. Secondly, thermally the processed drying oils, air dried (i.e. without stoving), are to some extent thermoplastic. This is why cores bonded only by a processed drying oil have to be stoved prior to casting.

Also, non-drying oils containing hydroxyl groups, like castor oil, when reacted in the presence of catalysts like tin salts and tertiary amines with polyisocyanates like diphenyl methane diisocyanate are slow setting and give a mould or core which is not strong enough.

By combining the two physico-chemical processes of drying and polyurethane formation a way of setting a foundry sand can be devised whereby both speed of setting and final strength can be controlled within wide limits.

Two catalysts are employed for controlling the setting of the moulds or cores. One of these catalysts is selected from the class of compounds usually employed as "driers"

for drying oils and consisting of the organic compounds of metals such as cobalt, manganese, tin, lead or zinc. Organic salts of cobalt are preferred, and cobalt octoate is most preferred. These catalysts are conveniently added as a solution in a solvent such as white spirit. The concentration of cobalt in a cobalt octoate solution in white spirit is preferably from 6% to 18% (based on the metal). This particular catalyst is preferred because it promotes both "drying" of the oil and condensation with the polyisocyanate.

The amount of a 6% solution of cobalt octoate in white spirit used in the binder may vary from 2% to 10% on the weight of blown linseed oil and blown tung oil according to speed of setting required. In practice 4% to 8% of the solution is used, i.e. a number of grades of oils having varying setting speeds may be prepared.

The cobalt octoate addition controls the speed of both physico-chemical reactions leading to hardening of sand mixed with the oil and polyisocyanate. This control is effective only within certain limits; the addition of cobalt octoate solution (6% of metal) above 10% on the oil will not speed up the setting appreciably. For example, a hydroxylated drying oil mixed with diphenylmethane diisocyanate in sand would produce compression specimen setting at ambient temperature of 20°C in about 24 hours. When the oil contains 4% of a 6% cobalt octoate solution the setting will take place in 2 hours. If the amount of cobalt octoate solution is raised to 8% the setting will occur in 1½ hours.

The other class of catalyst used in this invention is one frequently employed in polyurethane condensation reactions, namely the amines. A wide range of amines is available for this purpose and they differ considerably in their effect on the speed of reaction. Tertiary amines are the most effective and therefore preferred. Examples of these are: N,N - dimethylcetylamine, alkyl - dimethyl amines such as dimethyl hexadecylamine, dialkyl methyl amines such as dihexadecylmethylamine, triethanolamine and triethylamine.

We prefer to use triethylene diamine and N,N - dimethylphenethyl amine either separately or together.

Both the amine and the organic compound of the metal, preferably cobalt octoate, are necessary for really rapid setting. However, since the activity of the amine is gradually lost during storage of oil containing both catalysts, it is preferred to add one or other of the catalysts to the oil immediately before mixing with the other components of the foundry mix, or to add it as a separate component. It is convenient to mix the metal compound with the oil initially, rather than

the amine. The amount of amine employed will vary with the speed of setting required, and the actual amine. For example, not less than 0.2% and up to 1% of triethylene diamine may be used calculated on the blown oil.

It must be stressed that by using a tertiary amine and preferably mixing it separately into the sand, a much better degree of speed control can be achieved than if a metal compound only were used. To illustrate by example, an addition of 1% (an oil) of N,N-dimethylphenethylamine would reduce the setting figure of 1½ hours using cobalt octoate alone down to 20 minutes.

It will be apparent that the preferred method of applying the binder is similar to that already employed in foundry practice for "No Bake" furan resins. The binder is prepared as a two and preferably a three component system. One component comprises the hydroxylated drying oil usually in admixture with one of the chosen catalysts preferably cobalt octoate. The second component is the polyisocyanate. The third component is the other of the chosen catalysts preferably a tertiary amine. The preferred properties of the oil to ensure adequate bond formation are an initial iodine value not less than 150, and preferably 180 (during blowing the iodine value drops, but it should finally be not less than 40 preferably 80), and an hydroxyl value of processed oil not below 30 and preferably above 60. The oil should be processed according to the exact properties required.

The preferred oil is blown linseed oil mixed with blown tung oil. They can be either blown together or separately and then blended or first blown separately and then finished together. Other oils which may be used include processed oiticica or fish oil.

The preferred polyisocyanate is a diphenyl-

methane diisocyanate e.g. 4,4'-diphenylmethane diisocyanate but any polyisocyanate commonly used in the preparation of polyurethane polymers may be used.

If desired, the binder may be modified in such a way as to produce in the sand mix when applied, a preliminary ("green") bond. This enables the core maker to strip the core box straight after making the core, thereby increasing the turnout of cores per box. The cores thus produced would achieve the final strength required for casting in the normal way in due time, i.e. after 24 hours.

The formation of the green bond can be controlled according to requirements and it can be achieved in one or more of the following ways:

a) By premixing into the oil a small part of polyisocyanate a day or so before the binder is used. This will produce a considerable thickening of the binder until a "semi-solid"—jelly like consistency is reached. At this stage, when all the polyisocyanate has been combined, no further change will occur in the oil, this material when mixed with sand and the bulk of the polyisocyanate will give the sand a green bond. By adjusting the amounts of polyisocyanate initially reacted and the conditions the strength of the bond may be lower or higher.

b) By jellifying part of the oil by addition of a chloride of iron or aluminium.

Each of these ways (or a combination of them) can produce a desirable green bond without an appreciable lowering, of the final strength of the slowly setting core.

The invention will now be illustrated in the following non-limitative Examples, in which quantities are expressed by weight.

#### EXAMPLE 1

A green bond mix was prepared from the following:

A	{	Dry Silica sand	100	parts
		30 poise blown linseed oil	93.75	
		6% metal solution of Co octoate	4	1.5 parts
		N,N-dimethylphenethylamine	.25	
		4,4'-Diphenylmethane Diisocyanate	2	

#### B 4,4'-Diphenylmethane Diisocyanate

0.5 parts

Part A must age before mixing into sand; not less than 1 not more than 45 days.

#### EXAMPLE 2

A mix for quick setting was prepared as follows:

A	{	Dry silica sand	100	parts
		10 poise blown linseed oil	63.7	
		10 poise blown tung oil	20	1.5 parts
		6% (metal) cobalt octoate solution	6	
		White spirit	10.0	

B	4,4'-Diphenylmethane Diisocyanate	0.5 parts	10 poise blown linseed oil	0—95	10
C	N,N-dimethylphenethylamine	0.015 parts	10 poise blown tung oil	95—0	
5	Excellent results are obtained using the ingredients of Part A in the following range of properties:		6% (metal) cobalt octoate solution	4—8	
			White spirit	0—30	

## EXAMPLE 3

Another quick setting mix was prepared from the following: 15

20	A	{	Dry Silica sand	}	100 parts
			10 poise blown linseed oil 21.75		
			5 poise blown tung oil 50		
			6% metal cobalt octoate solution 8		
			White spirit 20		
			N,N-dimethylphenethylamine .25		1.5 parts

B	N,N-dimethylphenethylamine	.015 parts
25 C	4,4'-Diphenylmethane Diisocyanate	.5 parts

## WHAT WE CLAIM IS:—

1. A method in which a foundry mould or core is made by mixing sand and/or other refractory material with a binder and the mixture allowed to set and in which, as binder, there is used a blown drying oil and a polyisocyanate and the curing of the binder is catalysed by two catalysts, one of which is an organic compound of a metal and the other of which is an amine.

2. A method according to claim 1 wherein one of the catalysts is initially present in the oil, and the other is added separately during or just prior to mixing with the sand.

3. A method according to claim 2 wherein the amine is added separately.

4. A method according to any of claims 1 to 3 wherein the blown drying oil is a mixture of blown linseed oil and blown tung oil.

5. A method according to any of the preceding claims wherein the polyisocyanate is a diphenylmethane diisocyanate.

6. A method according to any of the preceding claims wherein the metal compound is cobalt octoate.

7. A method according to any of the preceding claims wherein the amine is a tertiary amine.

8. A method according to claim 7 wherein the tertiary amine is triethylene diamine or N,N-dimethylphenethyl amine or mixtures thereof.

9. A method according to claim 1 of making a foundry mould or core, substantially as described herein employing a mixture according to any of the Examples.

10. Foundry moulds and cores whenever made by a method according to any of the preceding claims.

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